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What does the global mean OH concentration tell us?

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Abstract. The global mean OH concentration ($[\text{OH}]_{\text{GM}}$) has been used as an indicator of the atmospheric oxidizing efficiency and its changes over time. It is also used for evaluating the performance of atmospheric chemistry models by comparing with other models or with observationally-based reference $[\text{OH}]_{\text{GM}}$ levels. We contend that the treatment of this quantity in the recent literature renders it problematic for either of these purposes. Several different methods have historically been used to compute $[\text{OH}]_{\text{GM}}$: weighting by atmospheric mass or volume, or by the reaction with CH_4 or CH_3CCl_3 . In addition, these have been applied over different domains to represent the troposphere. While it is clear that this can lead to inconsistent $[\text{OH}]_{\text{GM}}$ values, to date there has been no careful assessment of the differences expected when $[\text{OH}]_{\text{GM}}$ is computed using various weightings and domains. Here these differences are considered using four different 3D OH distributions, along with the weightings mentioned above applied over various atmospheric domains. We find that the $[\text{OH}]_{\text{GM}}$ values computed based on a given distribution but using different domains for the troposphere can result in differences of 10% or more, while different weightings can lead to differences of up to 30%, comparable to the uncertainty which is commonly stated for $[\text{OH}]_{\text{GM}}$ or its trend. Thus, at present comparing $[\text{OH}]_{\text{GM}}$ values from different studies does not provide clearly interpretable information about whether the OH amounts are actually similar or not, except in the few cases where the same weighting and domain have been used in both studies. We define the atmospheric oxidizing efficiency of OH with respect to a given gas as the inverse of the lifetime of that gas, and show that this is directly proportional to the $[\text{OH}]_{\text{GM}}$ value weighted by the reaction with that gas, where the proportionality constant depends on the temperature distribution and the domain. We find that the air-mass-weighted

and volume-weighted $[\text{OH}]_{\text{GM}}$ values, in contrast, are generally poor indicators of the global atmospheric oxidizing efficiency with respect to gases such as CH_4 and CH_3CCl_3 with a strong temperature dependence in their reaction with OH. We recommend that future studies provide both the air-mass-weighted and the CH_4 -reaction-weighted $[\text{OH}]_{\text{GM}}$ values, over the domain from the surface to a climatological tropopause. The combination of these values helps to reduce the chance of coincidental agreement between very different OH distributions. Serious evaluations of modeled OH concentrations would best be done with air-mass-weighted $[\text{OH}]_{\text{GM}}$ broken down into atmospheric sub-compartments, especially focusing on the tropics, where the atmospheric oxidizing efficiency is the greatest for most gases.

1 Introduction

The hydroxyl radical, OH, plays a critical role in the chemistry of the earth's troposphere. The earliest recognition of its importance came over three decades ago (Levy, 1971), and since then has grown considerably. OH is responsible for most of the breakdown of CH_4 and CO, particularly in the tropics (Crutzen and Zimmermann, 1991; Crutzen et al., 1999), and initiates the breakdown of most non-methane hydrocarbons (NMHCs) (e.g. Atkinson, 2000). When these oxidation chains occur in the presence of sufficient levels of nitrogen oxides, photochemical production of O_3 results (Crutzen, 1972, 1973, 1974; Chameides and Walker, 1973). OH also provides one of the major gas phase reaction pathways for SO_2 and dimethylsulphide (e.g. Yin et al., 1990), and thereby influences the atmospheric sulphur cycle, as well as aerosol and cloud particle formation (e.g. Kiehl et al., 2000). Likewise, it is a major factor in the removal of reactive nitrogen, via reaction of OH with NO_2 to form the highly soluble gas HNO_3 , which is readily removed by precipitation (Crutzen and Lawrence, 2000). While other reactive gases,

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in particular Cl, NO₃, and O₃, can play important secondary roles, OH stands out as the most important oxidant in the troposphere. The main source of OH is the reaction of excited atomic oxygen (from the photolysis of O₃) with water vapor, and its main sink is the reaction with CO, with important contributions from the reaction with CH₄ and other hydrocarbons.

Because of its primary role in initiating atmospheric oxidation chains, the global mean OH level, [OH]_{GM}, has been used as a metric for the atmospheric oxidizing efficiency. There are various possible definitions of the “oxidizing efficiency”, “oxidizing capacity”, “oxidizing power”, etc. For the purposes of this study, *OE_X*, the oxidizing efficiency of OH with respect to a gas *X*, will be defined as the rate of removal of a gas *X* from some atmospheric domain due to reaction with OH relative to the amount of the gas in that domain. The inverse of this quantity for a gas in steady state is often termed the “turnover time” (Bolin and Rodhe, 1973) or the “lifetime” (e.g. Brasseur et al., 1999) of the trace gas, although various definitions have also been applied to these terms (see the comments by Krol (2001) and our reply for further details); here we will employ the term lifetime.

Ideally, then, [OH]_{GM} should have some consistent relationship to the lifetime of a given gas in order to be a good indicator of the oxidizing efficiency with respect to that particular gas. There are several different ways to compute [OH]_{GM}, for instance, weighting by atmospheric mass or volume, or by the reaction with long-lived tracers such as methane (CH₄) and methylchloroform (1,1,1 trichloroethane, CH₃CCl₃, or “MCF”). These various techniques can yield very different values of [OH]_{GM}. To illustrate this, consider the extreme example of two OH distributions with the same total number of OH molecules in the troposphere, but where one has OH concentrated mainly in the tropics, while the other has the most OH in the extratropics. These two OH distributions will have the same volume-weighted [OH]_{GM} values. However, since reaction rates are generally temperature dependent, they will have very different [OH]_{GM} values if they are instead calculated by weighting with the reaction rate of CH₄ or CH₃CCl₃, and will also clearly result in different lifetimes of these gases. Similarly, the domain considered, particularly the vertical extent defining the troposphere, can also influence the relationship between [OH]_{GM} and *OE_X*. For instance, since OH is usually less concentrated in the upper troposphere than lower down, integrating from the surface to 100 hPa versus only integrating to 200 hPa can lead to notable changes in the air-mass- and volume-weighted [OH]_{GM} values, as well as in trace gas lifetimes.

In a brief survey of recent literature, we have found that a wide variety of weightings and domains have been employed to compute [OH]_{GM}; the survey results are summarized in Table 1 (the authors welcome further information about [OH]_{GM} values published since 1990 which are not included in this table, as well as information on the weight-

ings/domains which have been used). Table 1, along with the values to be discussed later in Table 2, provides the most extensive comparison of recent published [OH]_{GM} values of which we are aware. There are several factors which lead to the range of numbers in Table 1, and which make them difficult to compare. First, different techniques are used to compute the global OH distributions on which each [OH]_{GM} value is based, for instance, using a 3D chemistry-transport model, using kinetic box models constrained by observations of key parameters (e.g., O₃, CO), and using the inferred loss rate of CH₃CCl₃ based on its emissions, distribution and trend. Second, the basic parameters which are used in each of these techniques, such as reaction rates, photolysis rates, and the calibration of CH₃CCl₃ measurements, are subject to change over time (in particular, the latter parameter changed notably in the mid-1990’s). Third, there are unresolved issues regarding the factors which control OH levels, for instance, the role of ship emissions of NO in potentially enhancing OH concentrations (Lawrence and Crutzen, 1999; Kashibhatla et al., 2000), and the role of convective transport of HO_x precursors to the upper troposphere (e.g. Jaeglé et al., 2001). Finally, the weightings and domains chosen to compute [OH]_{GM} will influence the results. This study focuses on determining the magnitude of influence of the latter factor; the first two issues will need to be considered in future studies.

Nearly every study listed in Table 1 uses a different combination of weighting and domain for computing [OH]_{GM}. The four main weighting factors which have been used are atmospheric mass, volume, and the reaction rates with CH₄ and CH₃CCl₃; others, for instance CH₃CCl₃ mass (Prinn et al., 1995, 2001), have also been used. The domain is usually below either the 100 hPa or 200 hPa pressure level, or some sort of latitudinally dependent tropopause, though other domains have also been used. Nevertheless, despite the potential differences pointed out in the example above, the manner in which [OH]_{GM} was computed is not always clear: out of 18 papers, only about half stated clearly how [OH]_{GM} was weighted, while in the rest this information either could not be found, or was not completely clear (note that for several of these, the weighting which was actually used was determined by personal communication with the authors). This has occurred despite the fact that Prather and Spivakovsky (1990) pointed out that “it is misleading to report a single ‘global average OH concentration (<OH>)’ without qualifying it as to the averaging kernel”. It is interesting to note that the weighting used is more frequently stated in recent papers than in older papers, and that several of the most recent studies also give [OH]_{GM} values for more than one method of computation (Prinn et al., 2001; Spivakovsky et al., 2000; Poisson et al., 2000; Wang et al., 1998).

Given this wide variety of weightings and domains, a direct interpretation of the results would be difficult. The comparability of these numbers depends on exactly how much of a difference it makes when different weightings and domains

Table 1. Survey of recently published values of $[\text{OH}]_{GM}$ ($\times 10^6$ molec/cm³)

Reference	$[\text{OH}]_{GM}$	Weighting ^a	Domain
(Spivakovsky et al., 1990)	0.8	Mass	below 100 hPa
(Prather and Spivakovsky, 1990) ^b	0.8	Mass	below 100 hPa
	0.65	Volume	
	1.05	CH ₄	
	1.06	MCF	
(Crutzen and Zimmermann, 1991)	0.7	Mass ^c	below 100 hPa
(Hough, 1991)	0.83	?	troposphere ^d
(Prinn et al., 1995)	0.97 (± 0.06)	MCF-Mass ^{c,e}	below 200 hPa
(Derwent, 1996)	1.2	?	0–12 km
(Berntsen and Isaksen, 1997)	1.1	Volume ^f	below $\sigma = 0.152$
(Collins et al., 1997)	1.4 ^g	Volume	below ~ 89 hPa ^h
(Hein et al., 1997)	1.03	MCF	troposphere ⁱ
(Krol et al., 1998) ^j	1.07 ^{+0.09} _{-0.17}	Volume ^c	below 100 hPa
(Wang et al., 1998)	1.0	Mass	below 200 hPa
	1.2	MCF	
(Karlsdottir and Isaksen, 2000)	1.01 ^k	?	?
(Montzka et al., 2000)	1.1 (± 0.2)	MCF	below ~ 180 hPa ^l
(Poisson et al., 2000) ^m	1.24	Mass	below 100 hPa
	1.56	CH ₄	
(Roelofs and Lelieveld, 2000)	1.00 ⁿ	Volume ^c	troposphere ^o
(Spivakovsky et al., 2000)	1.16 (± 0.17) ^p	Mass	0–32° lat: below 100 hPa; >32° lat: below 200 hPa
(Prinn et al., 2001)	0.94 \pm 0.13	Mass ^q	below 200 hPa
(Wang et al., 2001)	0.9	?	?

^a “Volume” and “Mass” imply weighting by the atmospheric volume or airmass (or density), “CH₄” and “MCF” imply weighting by the product of their mass and reaction rate with OH (Eq. 1 and 2)

^b Based on the same OH distribution as in (Spivakovsky et al., 1990); the CH₄ and MCF reaction weighted values assume a uniform distribution for these two gases; values were also given for hypothetical gases with temperature dependences of $\exp(-1000/T)$ and $\exp(-2300/T)$ in their reaction rate coefficients with OH, yielding $[\text{OH}]_{GM}$ values of 0.96 and 1.11×10^6 molec/cm³, respectively

^c Based on Personal Communication (not stated explicitly in the original publication)

^d Not clearly defined

^e Weighted only by CH₃CCl₃ mass, not the reaction rate; in the paper this was referred to as the “temperature and atmospheric density-weighted average”

^f Called the “arithmetic mean”, presumed to imply volume weighted

^g Mean of the values given for Feb. (1.39×10^6 molec/cm³) and Aug. (1.41×10^6 molec/cm³)

^h Below hybrid coordinate level $\eta = 0.1$

ⁱ Tropics: below model level centered at 200 hPa, Extratropics: below model level centered at 320 hPa

^j Values for 1993 given here; 1978 value was $1.00^{+0.09}_{-0.15}$

^k 1996 value taken from their Fig. 2, ranges from 0.95 in 1980 to 1.01 in 1996

^l The tropospheric mass is assumed to be 0.82 of the total atmospheric mass, implying an upper bound of approximately 180 hPa

^m Values with NMHCs given here, without NMHCs the values were 1.45 and 1.81, respectively

ⁿ Value with NMHCs given here, without NMHCs it was 1.08

^o Defined based on thresholds for the potential vorticity and lapse rate

^p Range based on the maximum uncertainty estimate of 15%

^q Nearly the same value (0.93) was found for the CH₃CCl₃ mass-weighted (not reaction-weighted) mean OH concentration

are applied in calculating $[\text{OH}]_{GM}$. The illustrations given above make it clear that large differences are certainly possible; the more crucial question is: are the differences likely

to be significant in light of other uncertainties in computing $[\text{OH}]_{GM}$, given what we know about the global OH distribution? We examine this question here from the perspec-

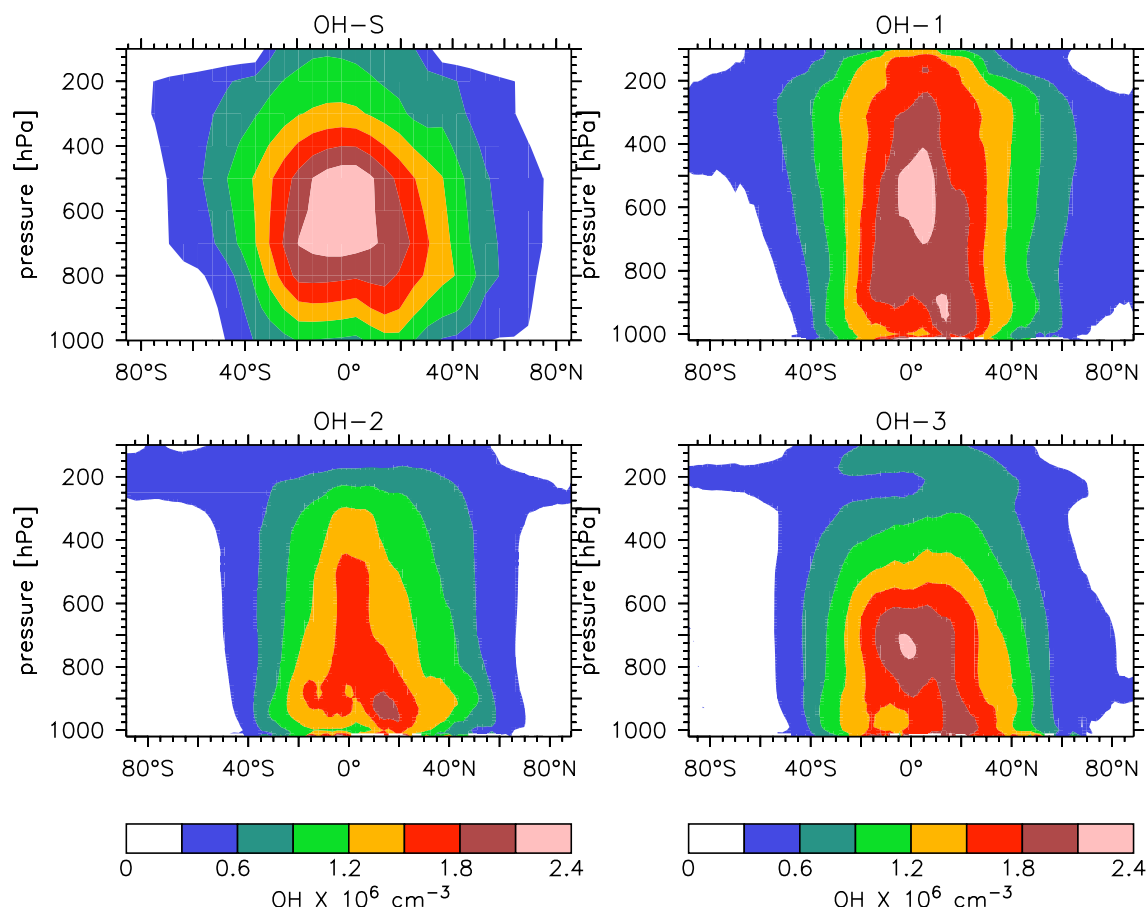


Fig. 1. The annual zonal mean OH fields based on the four distributions considered here: (a) OH-S (Spivakovsky et al., 2000); (b) OH-1 (Lawrence, 1996); (c) OH-2 (Lawrence et al., 1999); and (d) OH-3 (von Kuhlmann, 2001). The zonal mean values are computed by weighting every grid cell around a latitude band evenly, which is default for our plotting programs, and presumably for most others. Note, however, that the same arguments discussed in the text apply here: different plots could be produced by computing the zonal OH levels differently, e.g., weighting by the reaction with CH₄.

tive of understanding what the global mean OH concentration tells us about the atmospheric oxidizing efficiency with respect to important trace gases, in particular CH₄, as well as CH₃CCl₃, and how we can best go about comparing OH levels with this in mind. To do so, we consider $[\text{OH}]_{\text{GM}}$ based on four different 3D OH distributions, using several of the various weightings and domains encountered in Table 1. The four OH distributions chosen for this study are described in the next section; they can be considered representative of the range of characteristic distributions found in the recent literature. In Sect. 3, we discuss the various techniques used to compute $[\text{OH}]_{\text{GM}}$, and the physical interpretation of each of these, in particular their relationship to trace gas lifetimes. Section 4 considers the influence of different weighting factors on $[\text{OH}]_{\text{GM}}$ values computed for the four distributions; Section 5 considers the same for different domains. Sections 6 and 7 examine the regional distribution of CH₄ and CH₃CCl₃ oxidation in the troposphere, and how this can be used to help choose a set of subdomains appro-

priate for future comparisons of OH distributions. Section 8 gives our conclusions and recommendations for future studies.

2 OH fields description

We examine $[\text{OH}]_{\text{GM}}$ using four different global OH distributions. The first one, OH-S, is from the empirical analysis of Spivakovsky et al. (2000), which gives the OH distribution on an $8^\circ \times 10^\circ$ grid in pressure intervals of 100 hPa. Their OH levels are computed based on a photochemical box model combined with observed distributions of the main parameters influencing local OH, e.g., O₃, H₂O, CO, NO_x, hydrocarbons, and solar radiation. The other three global OH distributions used here, OH-1, OH-2, and OH-3, were computed using the global 3D chemistry-transport model MATCH (Model of Atmospheric Transport and Chemistry; Rasch et al. (1997), in its extended configuration MATCH-

MPIC (Max-Planck-Institute for Chemistry version), which includes tropospheric chemistry; output from three different versions are used here (OH-1 is from MATCH-MPIC 1.2, Lawrence (1996); OH-2 is from MATCH-MPIC 2.0, Lawrence et al. (1999); OH-3 is from MATCH-MPIC 3.0, von Kuhlmann (2001)). All three of these were computed at a relatively high horizontal resolution of about 2×2 degrees (T63), with 28 sigma levels between the surface and about 2 hPa. An extensive discussion of the testing of three of these distributions (all but OH-3) using various tracers such as CH_3CCl_3 and ^{14}CO is given by Jöckel (2000). There were numerous differences between the three MATCH-MPIC model versions, in particular the inclusion of non-methane hydrocarbon reactions in computing OH-3 (OH-1 and OH-2 are based on CH_4 -only chemistry), along with other major modifications, such as the advection and convection schemes, several emissions fields, and a few key reaction rates, resulting in rather different OH fields (see Lawrence et al. (1999) and von Kuhlmann (2001) for more details).

The annual zonal mean OH levels based on these four distributions are shown in Fig. 1; these and all values discussed here are day and night (24-hour) means, rather than daytime-only means (OH concentrations are very low at night compared to day). OH-S is largely hemispherically symmetric, while OH-1, OH-2, and OH-3 have notably more OH in the northern hemisphere. OH-S, OH-1, and OH-3 have the highest zonal mean OH levels in the tropical mid-troposphere, peaking at about 2.3×10^6 molec/cm³ in both, at a somewhat higher altitude (600 hPa) in OH-S and OH-1 than in OH-3 (700 hPa). The OH-2 distribution has a maximum much closer to the surface, and the peak value is lower, around 1.8×10^6 molec/cm³. The OH-2 distribution resembles another recent study focused on global OH (Krol et al., 1998), while some other models (e.g. Crutzen and Zimmermann, 1991; Wang et al., 1998) compute OH distributions which more closely resemble the OH-S distribution. Although we focus mainly on vertical differences here, there are also important horizontal differences; in particular, OH is depleted over the forested tropical continents in the OH-3 and OH-S distributions, due to the influence of isoprene and other NMHCs on OH in source regions, in contrast to OH-1 and OH-2 (which do not include the effects of NMHCs). These four distributions are used in this study in an effort to represent much of the range of recent estimates of the global OH distribution.

3 Computing the global mean OH concentration

$[\text{OH}]_{\text{GM}}$ is generally computed from a 2D or 3D OH distribution by applying some type of weighting factor, W :

$$[\text{OH}]_{\text{GM}} = \frac{\sum(W \cdot [\text{OH}])}{\sum W}, \quad (1)$$

where the summation is over all grid cells in a chosen region (e.g., the troposphere). The weighting factor W can take on

different forms. Often either the air mass or the volume are used. The volume-weighted variant (hereafter $[\text{OH}]_{\text{GM}}(\text{V})$) is the literal interpretation of a global mean concentration: all OH molecules spread over the total volume of the troposphere. We therefore assume it is likely that some of the studies in Table 1 which did not state the weighting that was used were adopting this literal definition, and thus considered it to be superfluous to specify how $[\text{OH}]_{\text{GM}}$ was computed. It is difficult, however, to assign a physical meaning to this quantity in terms of other relevant atmospheric parameters. The airmass-weighted value (hereafter $[\text{OH}]_{\text{GM}}(\text{M})$) can be considered as indicative of the oxidizing efficiency (or lifetime) for a uniformly-distributed gas with no temperature or pressure dependence in its reaction with OH (see Equations 2–5 below).

Alternatively, W can be chosen to provide information about the lifetime of a given gas X , in which case the global mean OH concentration (hereafter $[\text{OH}]_{\text{GM}}(X)$) is computed using:

$$W = k_X(T, P) \cdot M_X \quad (2)$$

where k_X is the reaction rate of OH with the gas X , usually temperature and/or pressure dependent, and M_X is the mass of the gas in a grid cell. X is generally chosen to be a long-lived gas which primarily reacts with OH, in particular CH_4 and CH_3CCl_3 . It is occasionally assumed that the distribution of some long-lived gases such as CH_4 and CH_3CCl_3 can be treated as uniformly distributed (e.g. Spivakovsky et al., 2000), so that an alternative weighting would be $W = k_X(T, P) \cdot M_{\text{air}}$, where M_{air} is the air mass. For the cases considered here, this assumption is generally very good, and leads to <1% error in the annual mean $[\text{OH}]_{\text{GM}}$ values (<5% for monthly values), compared to using M_X in Eq. 2.

In this study, we consider $[\text{OH}]_{\text{GM}}$ for four distinct weightings: air mass ($[\text{OH}]_{\text{GM}}(\text{M})$); volume ($[\text{OH}]_{\text{GM}}(\text{V})$); and the reaction rates with CH_4 and CH_3CCl_3 ($[\text{OH}]_{\text{GM}}(\text{CH}_4)$ and $[\text{OH}]_{\text{GM}}(\text{MCF})$, respectively; Eq. 2). For the temperature, air mass, and tracer mass fields (CH_4 and CH_3CCl_3) which are needed for these calculations, we employed the distributions from MATCH-MPIC version 2.0 (for information about the computation of CH_4 , see Lawrence et al. (1999); for details about CH_3CCl_3 emissions, which are the same as in Krol et al. (1998), and about its sinks, see Jöckel (2000)); note that we also tested using the fields from an earlier model version (MATCH-MPIC 1.2), and obtained essentially the same results.

As discussed in the introduction, we define the atmospheric oxidizing efficiency with respect to a given gas X to be the inverse of the lifetime ($\tau(X)$) of that gas

$$OE_X = \frac{1}{\tau(X)} \quad (3)$$

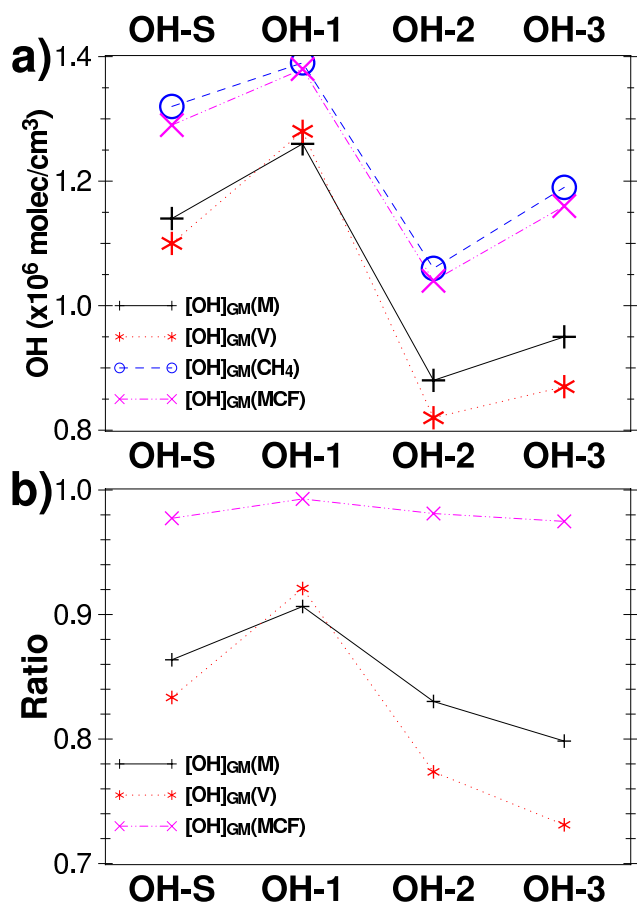


Fig. 2. Depictions of the relationships between different ways of computing the tropospheric $[OH]_{GM}$: (a) $[OH]_{GM}$ values for the four distributions and four weightings discussed in the text; (b) ratio of $[OH]_{GM}$ values for three weightings versus $[OH]_{GM}(CH_4)$.

where the lifetime is defined as:

$$\tau(X) = \frac{\Sigma M_X}{\Sigma(k_X \cdot [OH] \cdot M_X)} \quad (4)$$

Combining this with equations (1) and (2) for the reaction rate weighted mean OH ($[OH]_{GM}(X)$) yields:

$$\tau(X) = \alpha \cdot ([OH]_{GM}(X))^{-1} \quad (5)$$

where

$$\alpha = \frac{\Sigma M_X}{\Sigma(k_X \cdot M_X)} \quad (6)$$

Thus, for a well-mixed gas, $\tau(X)$ and $[OH]_{GM}(X)$ are inversely related by the coefficient α , whose value generally depends only on the temperature distribution in the atmosphere, the temperature dependence of the reaction, and the domain over which the summation is applied. For the CH₄ and CH₃CCl₃ distributions and reaction rates used here, integrated over the climatological troposphere domain defined below (Eq. 7), α (in yr·molec/cm³) is computed to

Table 2. Global annual mean tropospheric OH concentrations ($\times 10^6 \text{ molec/cm}^3$) for different OH distributions and weightings

Weighting Factor	OH-S	OH-1	OH-2	OH-3
Air Mass	1.14	1.26	0.88	0.95
Air Volume	1.10	1.28	0.82	0.87
CH ₄ Reaction	1.32	1.39	1.06	1.19
CH ₃ CCl ₃ Reaction	1.29	1.38	1.04	1.16

be 10.86 and 6.41, respectively. The same values (within roundoff) are computed assuming the gases are uniformly distributed. However, integrating over different domains results in considerably different values: below 300 hPa yields 9.54 and 5.71, below 200 hPa yields 10.47 and 6.20, and below 100 hPa yields 11.48 and 6.69. This is due to two factors. First, the $[OH]_{GM}(CH_4)$ and $[OH]_{GM}(MCF)$ values do not change much for different vertical domains, since the amount which reacts with CH₄ and CH₃CCl₃ in the upper troposphere is minimal (see Sect. 6), so that the UT is only weighted weakly. On the other hand, the lifetime is strongly dependent on the vertical extent over which it is computed; for example, extending the upper bound to a higher altitude does not add much to the total loss (in Tg/yr), but it does add to the tracer mass (in Tg). Thus, since in Eq. 5 $[OH]_{GM}(X)$ is relatively constant with altitude, whereas $\tau(X)$ varies notably, α must also vary strongly with the extent of the tropospheric domain.

Table 3. Global annual mean tropospheric lifetimes (years) for CH₄ and CH₃CCl₃

Gas	OH-S	OH-1	OH-2	OH-3
CH ₄	8.23	7.79	10.25	9.12
CH ₃ CCl ₃	4.95	4.66	6.16	5.50

4 Influence of the weighting factor on $[OH]_{GM}$

In this section the differences in $[OH]_{GM}$ values due to using different weightings will be discussed. $[OH]_{GM}$ based on the OH distributions and weightings discussed above are given in Table 2 and Fig. 2. The implied lifetimes for CH₄ and CH₃CCl₃ are also listed (Table 3).

Monthly mean fields (OH, CH₄, etc.) were used in these computations. Since temperatures are usually higher during the daytime, when OH concentrations are highest, one might expect higher $[OH]_{GM}$ values if hourly data were to be used in Equations 1 and 2 instead of monthly means. To test this effect we performed a 1-month run for March conditions at a reduced model resolution (T21, about 5.6 degrees in latitude

and longitude). When we use the hourly values in Eqs. 1 and 2 and then average to get the value of $[\text{OH}]_{\text{GM}}$ for the month, we get less than a 1% difference from when we instead simply use the 1-month mean values of $[\text{OH}]$ and T to compute $[\text{OH}]_{\text{GM}}$. Thus, we can confidently employ the monthly $[\text{OH}]_{\text{GM}}$ values based on monthly mean $[\text{OH}]$ and T fields, and then average these to yield annual means. Only the annual mean results are discussed here; values for individual months lead to the same conclusions as the annual means.

In this section, results are only considered for the domain below a climatological tropopause, defined as

$$p = 300 - 215(\cos(\phi))^2 \quad (7)$$

where p is the pressure in hPa, and ϕ is the latitude (see Jöckel (2000) for further discussion of this tropopause definition); differences due to the definition of the tropospheric domain are considered in the next section.

The spread ((maximum-minimum)/average) in $[\text{OH}]_{\text{GM}}$ calculated using the different weightings is about 18% for OH-S, 10% for OH-1, 25% for OH-2, and 31% for OH-3, comparable to or larger than the uncertainty ranges in $[\text{OH}]_{\text{GM}}$ stated by Spivakovsky et al. (2000), Krol et al. (1998), and Prinn et al. (1995, 2001). The results indicate that weighting by the reaction with CH_4 or CH_3CCl_3 always yields the highest values for $[\text{OH}]_{\text{GM}}$. This is due to the strong temperature dependence of these reactions, so that the tropics and the mid to lower troposphere, where OH concentrations are highest (Fig. 1), are weighted most strongly. $[\text{OH}]_{\text{GM}}(\text{M})$ and $[\text{OH}]_{\text{GM}}(\text{V})$ are generally closer to each other than to $[\text{OH}]_{\text{GM}}(\text{CH}_4)$ and $[\text{OH}]_{\text{GM}}(\text{MCF})$, though the relationship between the parameters is rather variable. The differences are smallest for OH-1, which is most evenly distributed in the vertical throughout the troposphere (Fig. 1). The other distributions, with OH falling off sharply in the tropical upper troposphere, show larger differences between the four different $[\text{OH}]_{\text{GM}}$ values, especially OH-2, which is weighted most strongly towards the surface, and OH-3, which falls off at lower altitudes in the tropics than the other distributions.

Figure 2b shows the ratio of $[\text{OH}]_{\text{GM}}(\text{M})$, $[\text{OH}]_{\text{GM}}(\text{V})$ and $[\text{OH}]_{\text{GM}}(\text{MCF})$ to $[\text{OH}]_{\text{GM}}(\text{CH}_4)$ for each of the four OH distributions. Recall that $[\text{OH}]_{\text{GM}}(\text{CH}_4)$ is directly related to the inverse of $\tau(\text{CH}_4)$ (Eq. 5), and thus to OE_{CH_4} . In order for any of the other three parameters to also serve as a good indicator of the oxidizing efficiency with respect to CH_4 which is applicable to any “typical” OH distribution, then they should have a consistent relationship to $[\text{OH}]_{\text{GM}}(\text{CH}_4)$, i.e., they should yield approximately horizontal lines on Fig. 2b. While $[\text{OH}]_{\text{GM}}(\text{MCF})$ essentially fulfills this criterion, the two “generic” parameters $[\text{OH}]_{\text{GM}}(\text{M})$ and $[\text{OH}]_{\text{GM}}(\text{V})$ clearly do not. The ratio between $[\text{OH}]_{\text{GM}}(\text{M})$ and $[\text{OH}]_{\text{GM}}(\text{CH}_4)$ differs by $>10\%$, while for $[\text{OH}]_{\text{GM}}(\text{V})$ the ratio varies by $>20\%$.

Although the principle behind the result in Fig. 2b is clear, since the relationship between OH amounts and OE_{CH_4} depends on the geographical distribution of OH, to date it has not been made clear how much the relationship between $[\text{OH}]_{\text{GM}}(\text{M})$, $[\text{OH}]_{\text{GM}}(\text{V})$ and $[\text{OH}]_{\text{GM}}(\text{CH}_4)$ (or $\tau(\text{CH}_4)$) should actually vary for current estimates of the OH distribution. Based on Fig. 2b we conclude that $[\text{OH}]_{\text{GM}}(\text{M})$ and $[\text{OH}]_{\text{GM}}(\text{V})$ are not very good indicators of the atmospheric oxidizing efficiency with respect to long-lived gases with strong temperature dependences such as CH_4 and CH_3CCl_3 , at least not on a global basis. However, when the atmosphere is broken down into smaller domains, over which the temperature and OH concentration do not vary as much, then the ability of the airmass- and volume- weighted regional mean OH values to represent the regional OE_{CH_4} (or OE_{MCF}) values improves considerably, as discussed in Section 7.

5 Influence of the tropospheric domain on $[\text{OH}]_{\text{GM}}$

In this section, the differences in $[\text{OH}]_{\text{GM}}$ computed over four different domains are considered: (1) the region below the climatological tropopause defined in Eq. 7, (2) the region below 100 hPa, (3) the region below 200 hPa, and (4) the region below 300 hPa. The first three represent the extremes of what is encountered in Table 1, while the latter is included because it is purely tropospheric, and contains the region where atmospheric gases like CH_4 and CH_3CCl_3 are mainly oxidized (discussed in the next section).

The ratios of $[\text{OH}]_{\text{GM}}(\text{M})$, $[\text{OH}]_{\text{GM}}(\text{V})$, $\tau(\text{CH}_4)$, and $\tau(\text{CH}_3\text{CCl}_3)$ for the latter three domains versus the values for the climatological troposphere are depicted in Fig. 3, which shows that the volume-weighted OH values are particularly strongly affected by the chosen domain, varying by 20% or more for the region below 100 hPa versus that below 300 hPa. The lifetimes of CH_4 and CH_3CCl_3 are almost as strongly affected, also varying by nearly 20%, while $[\text{OH}]_{\text{GM}}(\text{M})$ varies by about 10%. Restricting this to only the domains encountered in Table 1 (i.e., all but Fig. 3c), the differences are about 10% for $[\text{OH}]_{\text{GM}}(\text{V})$, $\tau(\text{CH}_4)$, and $\tau(\text{CH}_3\text{CCl}_3)$, and about 5% for $[\text{OH}]_{\text{GM}}(\text{M})$. The OH distribution which shows the least sensitivity to domain is OH-1, due to the relatively high tropical OH values extending vertically to about the 100 hPa level. In contrast, the variation in $\tau(\text{CH}_4)$ and $\tau(\text{CH}_3\text{CCl}_3)$ is similar for all four OH distributions, since the amount of tracer which is oxidized in the upper troposphere mainly depends on the rapidly falling temperature, rather than the OH values. On a similar note, the ratios of values for $[\text{OH}]_{\text{GM}}(\text{CH}_4)$ and $[\text{OH}]_{\text{GM}}(\text{MCF})$ are not shown in the figure, since they are all in the range 0.99–1.02. The reason for the weak dependence of these quantities on the chosen tropospheric domain, as discussed previously, is that very little oxidation of CH_4 and CH_3CCl_3 occurs in the upper troposphere, and thus the values in the region above 300 hPa are hardly weighted in computing $[\text{OH}]_{\text{GM}}(\text{CH}_4)$.

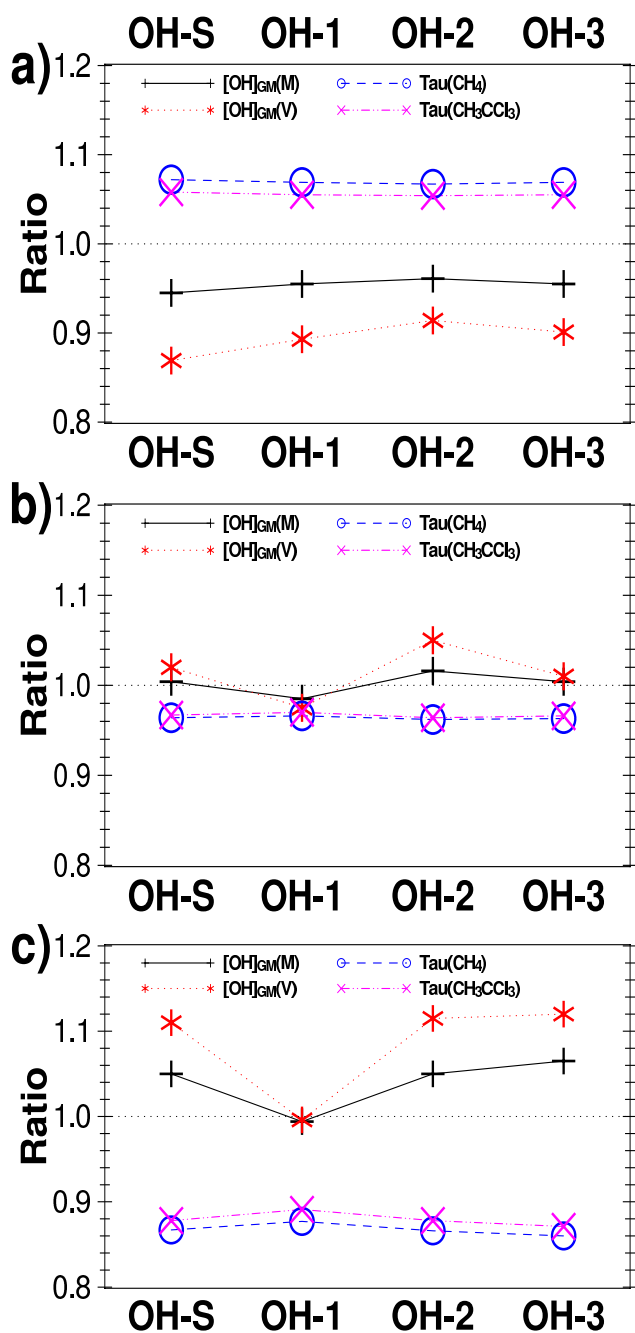


Fig. 3. The ratios of $[\text{OH}]_{\text{GM}}(\text{M})$, $[\text{OH}]_{\text{GM}}(\text{V})$, $\tau(\text{CH}_4)$, and $\tau(\text{CH}_3\text{CCl}_3)$ for (a) the domain below 100 hPa, (b) the domain below 200 hPa, and (c) the domain below 300 hPa, versus the values for the climatological troposphere (Eq. 7).

and $[\text{OH}]_{\text{GM}}(\text{MCF})$. This issue is considered further in the next section.

6 The distribution of CH_4 and CH_3CCl_3 oxidation in the troposphere

It has been well established in previous studies that CH_4 oxidation is weighted towards the tropics (e.g. Crutzen and Zimmermann, 1991; Crutzen et al., 1999); in addition, it is known that the lifetime of CH_4 increases significantly with altitude (e.g. Krol and van Weele, 1997). Because the vertical distribution of CH_4 oxidation plays an important role in the relationship between $[\text{OH}]_{\text{GM}}$ and OE_{CH_4} , as discussed above, we examine this in more detail here. In Fig. 4 we show the breakdown of the percentage of oxidation of CH_4 which occurs in selected subdomains of the atmosphere, where the breakdown is computed based on the OH distributions considered here. Figure 5 gives an overall impression of this breakdown as the average of the values for all four OH distributions in Fig. 4 taken over larger subdomains, along with the same summary information for CH_3CCl_3 .

The values in Fig. 4 are a reflection of the OH distributions in Fig. 1 and the temperature distribution in the atmosphere (along with the slight asymmetry in CH_4 , with $\sim 10\%$ more in the NH). We find that in the extratropics ($30^\circ\text{--}90^\circ$), more is oxidized in the NH than in the SH in all four of the distributions. The OH-S distribution yields an opposite asymmetry in the tropics, so that on the whole the amount of CH_4 oxidation (and the OH amounts) based on OH-S is roughly hemispherically symmetric; however, this results from the balance between the opposing asymmetries in the tropics and extratropics. The MATCH OH distributions, on the other hand, favor the NH in both the tropics and the extratropics. The north-south asymmetry has been discussed in several studies; often model results, such as those shown here, are in contradiction with observational evidence (e.g. Brenninkmeijer et al., 1992; Montzka et al., 2000). The reasons for this are currently unclear; one possible contributing factor is that the OH estimates based on CH_3CCl_3 observations are influenced by the fact that the ITCZ, which separates the meteorological NH and SH, lies on average a few degrees north of the equator (Montzka et al., 2000).

The summary in Fig. 5 shows the dominance of the tropical lower troposphere in the overall oxidation of CH_4 and CH_3CCl_3 , where on average $>60\%$ of the total oxidation occurs. The tropical mid troposphere, and the extratropical lower tropospheric regions, particularly in the NH, play secondary roles. The upper troposphere and stratosphere combined are responsible for $<10\%$ of the total oxidation of these gases, and the region above 250 hPa accounts for $<5\%$ of the total. This indicates that the focus on comparing mean OH concentrations, to the extent that these should be indicative of OE_{CH_4} or OE_{MCF} , should be on the lower and mid troposphere, particularly in the tropics.

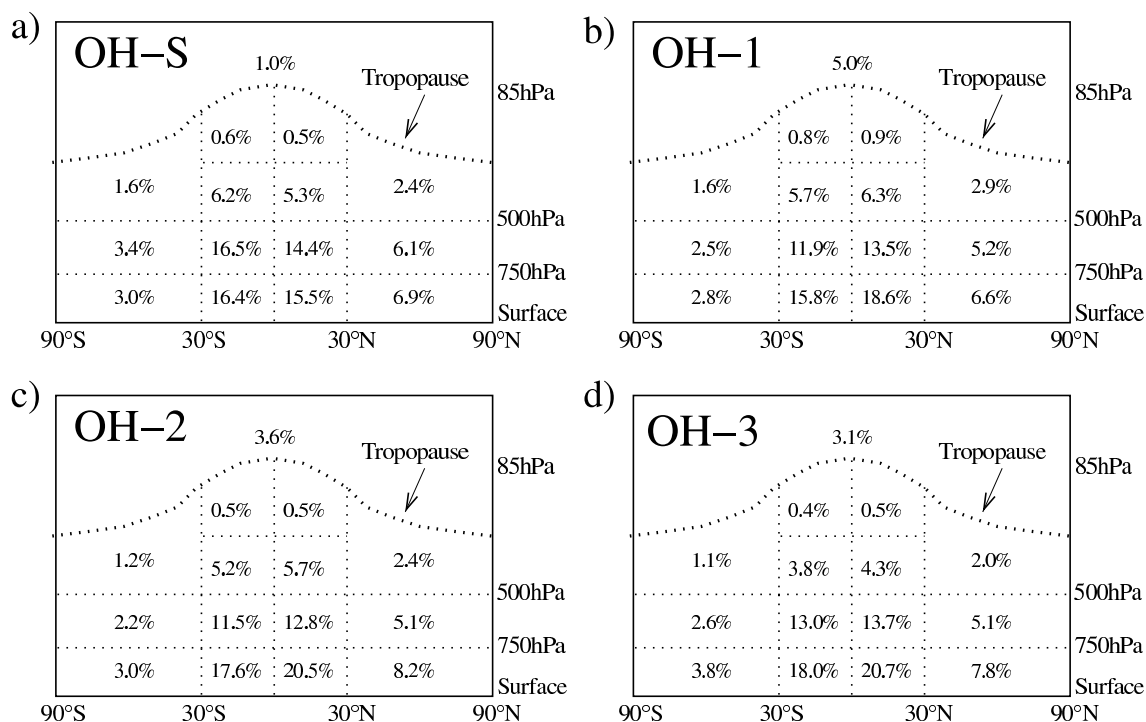


Fig. 4. The percentages of CH_4 which are oxidized in various subdomains of the atmosphere based on four different OH distributions: (a) OH-S; (b) OH-1; (c) OH-2; (d) OH-3. The horizontal lines in the tropical upper tropospheric regions are at 250 hPa.

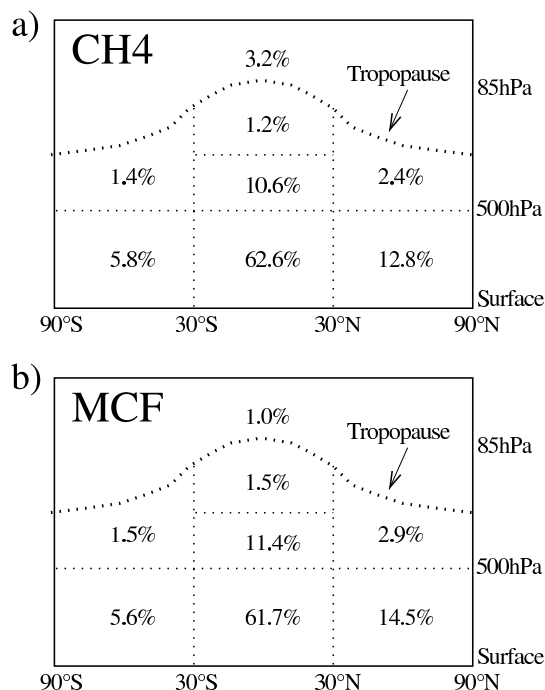


Fig. 5. The percentages of (a) CH_4 and (b) CH_3CCl_3 which are oxidized in various subdomains of the atmosphere based on the average of the four OH distributions (OH-S, OH-1, OH-2, and OH-3). Numbers may not add up to exactly 100% due to roundoff.

7 Atmospheric subdomains for comparing OH distributions

Figure 4 can be used to help devise a strategy for comparing modeled OH distributions. This should be a balance between: (1) sufficient information to really judge whether OH distributions are similar, at least in terms of their role in determining the atmospheric oxidizing efficiency; (2) manageability of the amount of numbers to compare, and (3) applicability to various model settings. In this regard, a generic parameter (airmass or volume weighted $[\text{OH}]$), rather than one tied to a specific gas (e.g., CH_4), would be desirable, since it would make the comparison less dependent on model parameters such as the temperature and trace gas distributions. However, as found above, this does not work well on a global basis, so that a breakdown into atmospheric subdomains needs to be considered.

We propose a breakdown in the horizontal at 30°S , 0° , and 30°N , following Prinn et al. (1995, 2001), and vertical divisions at 750, 500, and 250 hPa, which gives approximately equal masses in each of the 12 atmospheric compartments below 250 hPa (Krol, 2001). The importance of the vertical division at 750 hPa can be seen by comparing the OH-S results with the other results in Fig. 4. While the OH-1, OH-2, and OH-3 distributions have about 50% more CH_4 oxidation in the lowermost layer (surface–750 hPa) than in the middle layer (750–500 hPa), the OH-S distribution results in nearly

even amounts of oxidation in the two vertical domains. In this case, it would be clearly possible for the distributions to have similar air-mass- or volume-weighted mean OH concentrations in the larger region between the surface and 500 hPa, but very different oxidizing efficiencies with respect to CH_4 . We do not include the region above 250 hPa, since it was shown in the previous section to be responsible for less than 5% of the oxidation of gases such as CH_4 with strong temperature dependences in their reaction with OH. Since the lowest level of most contemporary models is not fixed at 1000 hPa, but instead has a variable surface pressure, the air-mass in the regions from the surface to 750 hPa will deviate slightly from the 3.3×10^{20} kg in each of the other regions; from south to north, for our model data we compute masses of 3.1, 3.4, 3.3, and 3.0×10^{20} kg for these four boxes.

For each of the 12 subdomains suggested here, the relationship between $[\text{OH}]_{RM}(\text{M})$ and $[\text{OH}]_{RM}(\text{CH}_4)$, where the subscript RM indicates the regional mean, is relatively constant; the same applies to $\tau(\text{CH}_4)$. In comparison to the spread of $>10\%$ seen in Fig. 2b, the mean spread in the ratio of $[\text{OH}]_{RM}(\text{M})/[\text{OH}]_{RM}(\text{CH}_4)$ for the four OH distributions broken down into each of these 12 regions is 3.1%, with a standard deviation of 1.0%. The spread in the volume weighted regional means ($[\text{OH}]_{RM}(\text{V})/[\text{OH}]_{RM}(\text{CH}_4)$) is somewhat worse, averaging $4.6 \pm 1.6\%$. Thus, the $[\text{OH}]_{RM}(\text{M})$ (and to a lesser extent $[\text{OH}]_{RM}(\text{V})$) values broken down into these regions can be considered as representative of OE_{CH_4} in each region, and should provide an appropriate test of modeled OH distributions.

8 Conclusions and recommendations

What does the global mean OH concentration tell us about modeled OH distributions and amounts and about the oxidizing efficiency of the atmosphere? We have shown in this study that the answer to this depends critically on the weighting which is used to compute this value, as well as the domain over which it is integrated. We found that differences in $[\text{OH}]_{GM}$, the global mean OH concentration, can be as large as 30% due to employing different weightings which have historically been used, and $>10\%$ for different domains. These numbers are comparable to the stated uncertainty in $[\text{OH}]_{GM}$ (e.g. Prinn et al., 2001; Spivakovsky et al., 2000; Krol et al., 1998). They are also significant in light of the consideration that all but a few of the values in Tables 1 and 2 lie within about 50% of each other (range 0.75–1.25 molec/cm³). Since widely varying studies tend to give $[\text{OH}]_{GM}$ values which lie within this relatively limited range, a meaningful comparison between $[\text{OH}]_{GM}$ from different studies can only be done with similarly-computed values. Otherwise it is difficult to determine whether any agreement in $[\text{OH}]_{GM}$ from different studies is coincidental or real. The same principle also applies to trends in $[\text{OH}]_{GM}$ values when they are computed using different weightings.

For example, consider the scenario in which the total number of OH molecules increases by a certain amount (say 1%/yr). This would lead to the same trend in the volume-weighted $[\text{OH}]_{GM}$ value, regardless of whether the increase occurs in the upper troposphere or near the surface. In contrast, the same increase would cause a larger trend in air-mass-weighted or CH_4 -reaction-weighted $[\text{OH}]_{GM}$ if it occurred near the surface than if it occurred higher up. However, it is important to note that trends are not always computed based on year-to-year differences in modeled annual mean OH distributions; these arguments will not apply, for instance, when the OH trend is computed by scaling to determine the CH_3CCl_3 loss rate (Krol, 2001).

In this study we have focused on how to compare OH distributions in light of their ability to serve as indicators of OE_X , the global oxidizing efficiency with respect to a given gas X , which we define as the inverse of $\tau(X)$, the lifetime of X . We showed that $[\text{OH}]_{GM}$ is directly proportional to OE_X (i.e., inversely proportional to $\tau(X)$) only when it is weighted by the reaction with X ($[\text{OH}]_{GM}(X)$), in which case the proportionality coefficient depends only on the domain of integration, the reaction rate coefficient, and the temperature distribution. In contrast to this, on a global basis neither the air-mass-weighted nor the volume-weighted $[\text{OH}]_{GM}$ values are very good indicators of the atmospheric oxidizing efficiency with respect to important long-lived gases such as CH_4 with strong temperature dependences in their reaction with OH, since they are not sensitive to the regions where temperatures are highest, and thus where oxidation reactions are fastest. However, when the atmosphere is broken down into smaller domains, over which $[\text{OH}]$ and the temperature vary less significantly, then it was shown that the air-mass-weighted regional mean OH concentration, $[\text{OH}]_{RM}(\text{M})$, can also serve as a good indicator of the regional oxidizing efficiency for such gases.

The findings in this study lead us to the following recommendations for future studies:

1. Global mean OH would best be given in two forms: weighted with the reaction with CH_4 (Eq. 2), and weighted with the air mass; the former provides a direct indication of the atmospheric oxidizing efficiency with respect to the most important greenhouse gas which is mainly removed by reaction with OH, and is rather insensitive to differences in the vertical extent of the tropospheric domain used in its computation; the latter is indicative of OE_X for a gas with no temperature dependence in its reaction with OH, and is more sensitive to the averaging domain; we suggest using the domain defined by the climatological tropopause given in Eq 7; the combination of these two values helps give an initial screening for when two OH distributions are different, even if their global mean values for one of these weightings is coincidentally similar;

2. Serious evaluations of modeled OH distributions should break down the OH distribution into regional mean air-mass-weighted values ($[\text{OH}]_{\text{RM}}(\text{M})$) in tropospheric subdomains, in particular the 12 which have been discussed here. For future comparisons, the $[\text{OH}]_{\text{RM}}(\text{M})$ values in each of these 12 subdomains for the four OH distributions considered here are given in Table 4.

In addition, the tropospheric lifetimes of CH_4 ($\tau(\text{CH}_4)$) and CH_3CCl_3 ($\tau(\text{MCF})$) can also be provided as additional parameters related to the OH distribution since they can be compared directly with independent estimates of their values (e.g., from analyses of source strengths, atmospheric burdens, and growth or decline rates); again, we recommend using the domain defined by the climatological tropopause given in Eq. 7.

The second recommendation is clearly a difficult one to adopt on a widespread basis, since it is generally desirable to have a single number, where possible, which indicates model performance. However, we feel it is critical that the distribution of OH be taken into consideration in this or a similar way in future studies. Concluding that a model simulation of OH is “reasonable” because the global mean OH concentration is in good agreement with that from another study can be misleading, since two OH distributions can readily have the same $[\text{OH}]_{\text{GM}}$ values computed using different weightings, but very different distributions (e.g., one more concentrated towards the surface than the other), which could result in different oxidizing efficiencies. Although we do not wish to single out any particular studies here, we have found several instances in the literature in which such comparisons of differently-computed $[\text{OH}]_{\text{GM}}$ values have been made (in some cases apparently inadvertently, due to misinterpretation of other studies where the weighting which was used was unclear).

Our proposal for a single number which indicates the degree of agreement between various OH fields, both in terms of their amounts and their distributions, is the RMS deviation between $[\text{OH}]_{\text{RM}}(\text{M})$ for two distributions in the 12 subdomains depicted in Table 4. For the MATCH-MPIC OH distributions relative to the OH-S distribution, these values are (in 10^6 molec/cm^3): 0.21 (OH-1), 0.37 (OH-2), and 0.33 (OH-3). When considered in light of the global mean values of order $1 \times 10^6 \text{ molec/cm}^3$, these RMS differences are relatively high; they are nearly twice as large as the mean deviations based on the global values in Table 2 (0.12, 0.26, and 0.17, respectively). Thus, since our proposed approach is sensitive to both the OH amounts and its distribution (particularly the differences in the tropical vertical distributions seen in Fig. 1), it provides much more information than simply comparing global means does about the degree to which various OH distributions agree or disagree.

We offer these recommendations as a starting point for discussion by the community, and are open to suggestions of alternate details regarding the recommendations or alternate

Table 4. Regional annual mean air-mass-weighted OH concentrations ($\times 10^6 \text{ molec/cm}^3$) for different OH distributions in the recommended subdomains

Region	OH-S	OH-1	OH-2	OH-2
Below 750 hPa, 90°S–30°S	0.47	0.44	0.35	0.51
Below 750 hPa, 30°S–0°	1.44	1.56	1.30	1.51
Below 750 hPa, 0°–30°N	1.52	1.86	1.52	1.76
Below 750 hPa, 30°N–90°N	0.76	0.86	0.79	0.86
750 - 500 hPa, 90°S–30°S	0.72	0.56	0.36	0.46
750 - 500 hPa, 30°S–0°	2.00	1.65	1.20	1.48
750 - 500 hPa, 0°–30°N	1.99	1.94	1.37	1.61
750 - 500 hPa, 30°N–90°N	0.88	0.91	0.65	0.72
500 - 250 hPa, 90°S–30°S	0.64	0.65	0.37	0.36
500 - 250 hPa, 30°S–0°	1.43	1.55	1.04	0.82
500 - 250 hPa, 0°–30°N	1.36	1.76	1.15	0.96
500 - 250 hPa, 30°N–90°N	0.64	0.95	0.59	0.52

approaches to those proposed here, as long a standard is defined by the community and adhered to so that values from different studies can be directly compared. There are a number of related issues which are in particular need of further consideration. First, we have focused on the oxidizing efficiency with respect to CH_4 and CH_3CCl_3 in this study, since they are important, long-lived gases with relatively uniform distributions in the troposphere. It is formally possible to define an oxidizing efficiency with respect to shorter-lived gases such as CO; however, this would be more difficult to interpret and particularly to compare between different studies, since the oxidizing efficiencies for such gases strongly depend on both the OH distribution and the distribution of the gas in question. This issue could be considered further in future studies. Another point which will need to be considered is how to handle updates in the rate coefficients of OH with CH_4 and other gases, which affects the lifetime and the $[\text{OH}]_{\text{GM}}(X)$ values computed based on a given OH distribution. Finally, we recommend that the atmospheric research community develop clear, broadly accepted definitions of the terms “oxidizing efficiency”, “oxidizing power”, “oxidizing capability”, and “oxidizing capacity”; various definitions have been used in the past (e.g. Thompson, 1992), and a working definition for the oxidizing efficiency has been proposed here.

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References

- Atkinson, R.: Atmospheric chemistry of VOCs and NO_x , *Atmos. Environ.*, 34, 2063–2101, 2000.
- Berntsen, T. K. and Isaksen, I. S. A.: A global three-dimensional chemical transport model for the troposphere, 1. model description and CO and ozone results, *J. Geophys. Res.*, 102, 21 239–21 280, 1997.
- Bolin, B. and Rodhe, H.: A note on the concepts of age distribution and transit time in natural reservoirs, *Tellus*, 25, 58–62, 1973.
- Brasseur, G. P., Orlando, J. J., and Tyndall, G. S.: *Atmospheric Chemistry and Global Change*, Oxford University Press, New York, 1999.
- Brenninkmeijer, C., Manning, M., Lowe, D., Wallace, G., Sparks, R., and Volz-Thomas, A.: Interhemispheric asymmetry in OH abundance inferred from measurements of atmospheric ^{14}CO , *Nature*, 356, 50–52, 1992.
- Chameides, W. L. and Walker, J. C. G.: A photochemical theory of tropospheric ozone, *J. Geophys. Res.*, 78, 8751–8760, 1973.
- Collins, W. J., Stevenson, D. S., Johnson, C. E., and Derwent, R. G.: Tropospheric ozone in a global-scale three-dimensional lagrangian model and its response to NO_x emission controls, *J. Atmos. Chem.*, 26, 223–274, 1997.
- Crutzen, P. and Zimmermann, P. H.: The changing photochemistry of the troposphere, *Tellus*, 43 AB, 136–151, 1991.
- Crutzen, P. J.: Gas-phase nitrogen and methane chemistry in the atmosphere, Report AP-10, University of Stockholm, 1972.
- Crutzen, P. J.: A discussion of the chemistry of some minor constituents in the stratosphere and troposphere, *Pure and Applied Geophysics*, 106–108, 1385–1399, 1973.
- Crutzen, P. J.: Photochemical reactions initiated by and influencing ozone in unpolluted tropospheric air, *Tellus*, 16, 47–56, 1974.
- Crutzen, P. J. and Lawrence, M. G.: The impact of precipitation scavenging on the transport of trace gases: A 3-dimensional model sensitivity study, *J. Atmos. Chem.*, 37, 81–112, 2000.
- Crutzen, P. J., Lawrence, M. G., and Pöschl, U.: On the background photochemistry of tropospheric ozone, *Tellus*, 51, 123–146, 1999.
- Derwent, R.: The influence of human activities on the distribution of hydroxyl radicals in the troposphere, *Phil. Trans. Roy. Soc. London A*, 354, 501–531, 1996.
- Hein, R., Crutzen, P. J., and Heimann, M.: An inverse modeling approach to investigate the global atmospheric methane cycle, *Global Biogeochem. Cycles*, 11, 43–76, 1997.
- Hough, A. M.: Development of a two-dimensional global tropospheric model: model chemistry, *J. Geophys. Res.*, 96, 7325–7362, 1991.
- Jaeglé, L., Jacob, D. J., Brune, W. H., and Wennberg, P. O.: Chemistry of HO_x radicals in the upper troposphere, *Atmos. Environ.*, 35, 469–489, 2001.
- Jöckel, P.: Cosmogenic ^{14}CO as a tracer for atmospheric chemistry and transport, Ph.D. thesis, Universität Heidelberg, <http://www.ub.uni-heidelberg.de/archiv/1426>, 2000.
- Karlsdottir, S. and Isaksen, I. S. A.: Changing methane lifetime: Possible cause for reduced growth, *Geophys. Res. Lett.*, 27, 93–96, 2000.
- Kashibhatla, P., Levy II, H., Moxim, W. J., Pandis, S. N., Corbett, J. J., Peterson, M. C., Honrath, R. E., Frost, G. J., Knapp, K., Parrish, D. D., and Ryerson, T. B.: Do emissions from ships have a significant impact on concentrations on nitrogen oxides in the marine boundary layer?, *Geophys. Res. Lett.*, 27, 2229–2232, 2000.
- Kiehl, J., Schneider, T., Rasch, P., Barth, M., and Wong, J.: Radiative forcing due to sulfate aerosols from simulations with the national center for atmospheric research community climate model, version 3, *J. Geophys. Res.*, 105, 1441–1457, 2000.
- Krol, M.: Interactive Comment on “What does the global mean OH concentration tell us?” by “M. G. Lawrence et al.”, *Atmos. Chem. Phys. Discuss.*, 1, S1–S5, 2001.
- Krol, M., van Leeuwen, P. J., and Lelieveld, J.: Global OH trend inferred from methyl-chloroform measurements, *J. Geophys. Res.*, 103, 10 697–10 711, 1998.
- Krol, M. C. and van Weele, M.: Implications of variations in photodissociation rates for global tropospheric chemistry, *Atmos. Environ.*, 31, 1257–1273, 1997.
- Lawrence, M. G.: Photochemistry in the Tropical Pacific Troposphere: Studies with a Global 3D Chemistry-Meteorology Model, Ph.D. thesis, Georgia Institute of Technology, 1996.
- Lawrence, M. G. and Crutzen, P. J.: Influence of NO_x emissions from ships on tropospheric photochemistry and climate, *Nature*, 402, 167–170, 1999.
- Lawrence, M. G., Crutzen, P. J., Rasch, P. J., Eaton, B. E., and Mahowald, N. M.: A model for studies of tropospheric photochemistry: Description, global distributions, and evaluation, *J. Geophys. Res.*, 104, 26 245–26 277, 1999.
- Levy, H.: Normal atmosphere: Large radical and formaldehyde concentrations predicted, *Science*, 173, 141–143, 1971.
- Montzka, S. A., Spivakovsky, C. M., Butler, J. H., Elkins, J. W., Lock, L. T., and Mondeel, D. J.: New observational constraints for atmospheric hydroxyl on global and hemispheric scales, *Science*, 288, 500–503, 2000.
- Poisson, N., Kanakidou, M., and Crutzen, P. J.: Impact of non-methane hydrocarbons on tropospheric chemistry and the oxidizing power of the global troposphere: 3-dimensional modelling results, *J. Atmos. Chem.*, 36, 157–230, 2000.
- Prather, M. J. and Spivakovsky, C. M.: Tropospheric OH and the lifetimes of hydrochlorofluorocarbons, *J. Geophys. Res.*, 95, 18 723–18 729, 1990.
- Prinn, R. G., Weiss, R. F., Miller, B. R., Huang, J., Alya, F. N., Cunnold, D. M., Fraser, P. J., Hartley, D. E., and Simmonds, P. G.: Atmospheric trends and lifetime of CH_3CCl_3 and global OH concentrations, *Science*, 269, 187–190, 1995.
- Prinn, R. G., Huang, J., Weiss, R. F., Cunnold, D. M., Fraser, P. J., Simmonds, P. G., McCulloch, A., Harth, C., Salameh, P., O'Doherty, S., Wang, R. J. J., Porter, L., and Miller, B. R.: Evidence for substantial variations of atmospheric hydroxyl radicals in the past two decades, *Science*, 292, 1882–1888, 2001.
- Rasch, P. J., Mahowald, N. M., and Eaton, B. E.: Representations of transport, convection and the hydrologic cycle in chemical transport models: Implications for the modeling of short lived and soluble species, *J. Geophys. Res.*, 102, 28 127–28 138, 1997.
- Roelofs, G.-J. and Lelieveld, J.: Tropospheric ozone simulation with a chemistry-general circulation model: Influence of higher hydrocarbon chemistry, *J. Geophys. Res.*, 105, 22 697–22 712, 2000.
- Spivakovsky, C. M., Yevich, R., Logan, J. A., Wofsy, S. C., McElroy, M. B., and Prather, M. J.: Tropospheric OH in a three-dimensional chemical tracer model: An assessment based on observations of CH_3CCl_3 , *J. Geophys. Res.*, 95, 18 441–18 471, 1990.

- Spivakovsky, C. M., Logan, J. A., Montzka, S. A., Balkanski, Y. J., Foreman-Fowler, M., Jones, D. B. A., Horowitz, L. W., Fusco, A. C., Brenninkmeijer, C. A. M., Prather, M. J., Wofsy, S. C., and McElroy, M. B.: Three-dimensional climatological distribution of tropospheric OH: Update and evaluation, *J. Geophys. Res.*, 105, 8931–8980, 2000.
- Thompson, A. M.: The oxidizing capacity of the earth's atmosphere: Probable past and future changes, *Science*, 256, 1157–1165, 1992.
- Von Kuhlmann, R.: Photochemistry of Tropospheric Ozone, its Precursors and the Hydroxyl Radical: A 3D-Modeling Study Considering Non-Methane Hydrocarbons, Ph.D. thesis, Johannes Gutenberg-Universität Mainz, Mainz, Germany, 2001.
- Wang, K.-Y., Pyle, J. A., Shallcross, D. E., and Larry, D. J.: Formulation and evaluation of IMS, an interactive three-dimensional tropospheric chemical transport model 2. model chemistry and comparison of modelled CH₄, CO, and O₃ with surface measurements, *J. Atmos. Chem.*, 38, 31–71, 2001.
- Wang, Y., Logan, J. A., and Jacob, D. J.: Global simulation of tropospheric O₃-NO_x-hydrocarbon chemistry, 2. model evaluation and global ozone budget, *J. Geophys. Res.*, 103, 10 727–10 755, 1998.
- Yin, F., Grosjean, D., and Seinfeld, J.: Photooxidation of dimethyl sulfide and dimethyl disulfide .1. mechanism development, *J. Atmos. Chem.*, 11, 309–364, 1990.